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(54) PHOTOCATALYST THIN FILM IN WHICH METAL IS SUPPORTED ON
TITANIUM OXIDE THIN FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a photocatalyst thin film which has high ability of removing harmful substances from air or water, which hardly elute metals and which can be manufactured at normal temperature on the surface of a base body from a wide variety of materials and to provide a method to easily and safely manufacture the photocatalyst thin film.

SOLUTION: The photocatalyst thin film contains at least one kind from Cu, Ag, Pt, Pd, Ni, Co, Fe, Ru, Zn and Rh deposited by ≥ 5 pmol.cm⁻² and ≤ 500 pmol.cm⁻² density on a titanium oxide thin film formed from an anatase titanium oxide dispersion liquid containing peroxy groups (TO sol) prepared by crystallizing a peroxotitanium solution. The photocatalyst thin film is manufactured by forming the titanium oxide thin film from the anatase titanium oxide dispersion liquid containing peroxy groups and depositing the metals on the film by a photoreduction method.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention can be manufactured at ordinary temperature and relates to the photocatalyst thin film excellent in the toxic substance removal in an offensive odor or the air.

[0002]

[Description of the Prior Art] If it irradiates with the light which has the wavelength of the energy more than the band gap in the particles of titanium oxide which is one of the

photocatalysts, by optical pumping, an electron will be produced in a conducting zone and an electron hole will be produced in a valence band. Since the decomposition reaction of the organic substance and mineral matter of a particle surface occurs, titanium oxide is used for environmental clean-ups, such as the atmosphere and water, and uses, such as antifouling and antibacterial properties, by the powerful oxidizing power of the electron hole produced by this optical pumping. In order to prevent scattering and an outflow, or in order to make separation from a processor easy, the photocatalyst grains used for such processing are fixed in a bigger base than photocatalyst grains, and are used as a photocatalyst body. Titanium oxide photocatalyst coating liquid is applied to a base, and simple methods of manufacturing such a photocatalyst body include the method of forming a titanium oxide photocatalyst thin film in a base surface.

[0003]. As titanium oxide photocatalyst coating liquid, are indicated by JP,9-71418,A or JP,10-67516,A. If the anatase-type-titanium-oxide sol containing a peroxo group obtained by crystallizing amorphous type titanium peroxide sol is used, The titanium oxide photocatalyst thin film aiming at the environmental clean-up of the interior of a room and the outdoors, and use for uses, such as antifouling and antibacterial properties, Being able to manufacture and provide for the surface of the broad base of construction material at ordinary temperature, the titanium oxide photocatalyst thin film which produced the anatase-type-titanium-oxide sol containing this peroxo group at ordinary temperature has the high photocatalyst performance. However, having considered the practical use as a charge of an environment purifying material, to develop the photocatalyst thin film in which the toxic substance removal ability in a nearby offensive odor or the air is higher than this photocatalyst thin film was desired.

[0004]On the other hand, the method of combining metal with a titanium oxide photocatalyst is known as a method of raising the activity of a titanium oxide photocatalyst. By manufacturing the sol of the compound titanium oxide particles which become JP,11-188270,A from a dissimilar metal and titanium by heating the compound titanium peroxide which consists of a dissimilar metal and titanium, and applying this to a base. The method of manufacturing the compound titanium oxide thin film with high photocatalyst performance which consists of a dissimilar metal and titanium is indicated. However, since some added metal may have become a defect in compound titanium oxide particles, the photocatalyst thin film manufactured by this method did not have the enough improvement in activity by metal addition.

[0005]Carry out the coat of the hydrogen-peroxide-solution solution of titania gel to JP,6-304237,A in the glass surface of the bulb of an electric light, and heating calcination is carried out, It is indicated about the manufacturing method of the deodorization light by which it is deodorization light characterized [covering at least with a kind of metallic film chosen from among platinum, rhodium, a ruthenium, palladium, silver, copper, and zinc on it].

By the electron and the oxidation reduction operation of an electron hole which were generated to the titanium oxide membrane on the glass surface of a bulb in response to the light from the inside or the outside of deodorization light, and operation of a metallic film, it is indicated that the decomposition removal of the malodorous substance in the air can be carried out effectively.

However, when the photocatalyst thin film manufactured by this method has the problem that the interaction of a metal tunic and a titanium oxide thin film is weak, for example, it

was used underwater, or when a photocatalyst thin film was rinsed, there was a problem that metal was eluted and activity fell.

[0006]

[Problem(s) to be Solved by the Invention]As a charge of an environment purifying material, the inside of the atmosphere and underwater toxic substance removal ability of this invention are high, and an object of this invention is for maintenance of the supported metal to provide a good photocatalyst thin film.

[0007]

[Means for Solving the Problem]That this invention persons should solve an aforementioned problem, as a result of inquiring wholeheartedly, anatase-type-titanium-oxide sol containing a peroxo group to a titanium oxide thin film produced and made. It discovered that photocatalyst activity with an expensive photocatalyst thin film which supported very little dissimilar metals is shown, that metale maintenance of this photocatalyst thin film is good, and that it could manufacture at ordinary temperature on the surface of a base of construction material with this broad photocatalyst thin film, and resulted in this invention.

[0008]To namely, a titanium oxide thin film which this invention produces anatase type titanium oxide dispersion liquid containing (1) peroxo group, and is made. A photocatalyst thin film currently more than $5 \text{ pmol}\cdot\text{cm}^{-2}$ supporting with density below $500 \text{ pmol}\cdot\text{cm}^{-2}$ at least one sort of metallic elements chosen from a group of Cu, Ag, Pt, Pd, nickel, Co, Fe, Ru, Zn, and Rh, (2) . It is characterized by a titanium oxide thin film containing a peroxo group 10% or less of not less than 100 ppm by a mole ratio to Ti. (1) a photocatalyst thin film of a statement, and (3) a photocatalyst thin film of (1) or (2) statements, wherein metallic elements currently supported are with a 1-nm or more mean particle diameter [20 nm or less] metal particles -- it comes out.

[0009]Hereafter, this invention is explained in detail. A titanium oxide thin film in this invention needs to be the film produced using anatase type titanium oxide dispersion liquid containing a peroxo group. This anatase type titanium oxide dispersion liquid is the anatase type titanium oxide dispersion liquid containing a peroxo group prepared by a method currently indicated by JP,9-71418,A or JP,10-67516,A. This anatase type titanium oxide dispersion liquid is a drainage system and neutral dispersion liquid.

[0010]The typical process of this anatase type titanium oxide dispersion liquid is as follows. If hydrogen peroxide solution is added and stirred after rinsing dispersion liquid, such as titanium hydroxide gel and titanium oxide, until contamination ion is no longer detected, a yellow peroxotitanic acid solution will be obtained. If heat-treatment of 40 hours - 2 hours is performed for an obtained yellow peroxotitanic acid solution in 85 °C - 200 °C, anatase type titanium oxide dispersion liquid containing a peroxo group will be obtained.

[0011]Since titanium oxide content of this anatase type titanium oxide dispersion liquid has the viscosity whose dispersibility is good and moderate 0.01% of the weight or more as it is 5 or less % of the weight, Since 0.01-micrometer or more a 3-micrometer titanium oxide thin film can be coated with various coating methods known from the former, such as a spin coat method and a dip coating method, it is desirable. This anatase type titanium oxide dispersion liquid contains only an anatase type as titanium oxide. This is checked by showing only a peak which belongs to anatase type titanium oxide, when this anatase type titanium oxide dispersion liquid is dried, titanium oxide powder is prepared and a

powder X diffraction is measured.

[0012] This anatase type titanium oxide dispersion liquid measures a powder X diffraction of titanium oxide powder produced by carrying out vacuum drying of the dispersion liquid at ordinary temperature. Since it has specific surface area with an expensive thin film obtained as particle diameter computed by Scherrer's formula based on half breadth of an acquired field (101) is not less than 5 nm 20 nm or less, it is desirable. A photocatalyst thin film of this invention needs to support at least one sort of metallic elements among Cu, Ag, Pt, Pd, nickel, Co, Fe, Ru, Rh, and Zn to a titanium oxide thin film. Since an element which normal electrode potential is high and even metal is easy to be returned especially is preferred, Pt, Rh, Pd, Cu, Ag, and Ru are preferred.

[0013] Metal carrying density of more than $5 \text{ pmol}\cdot\text{cm}^{-2}$ is below $500 \text{ pmol}\cdot\text{cm}^{-2}$, and more than $10 \text{ pmol}\cdot\text{cm}^{-2}$ is below $100 \text{ pmol}\cdot\text{cm}^{-2}$ preferably. Less than $5 \text{ pmol}\cdot\text{cm}^{-2}$ of improvement in activity is not enough as carrying density, and since condensation of metal particles will take place and an active site of titanium oxide will be covered when more than $500 \text{ pmol}\cdot\text{cm}^{-2}$, activity falls. Metal carrying density is computing the total quantity of Cu contained in an applied metal salt solution, Ag, Pt, Pd, nickel, Co, Fe, Ru, Rh, and Zn by breaking by a coated area. All of these elements are calculated as what was returned and became metal.

[0014] As for metal currently supported by photocatalyst thin film of this invention, it is preferred to be supported with a with a 1-nm or more mean particle diameter [20 nm or less] particle, and it is 10 nm or less in not less than 2-nm mean particle diameter more preferably. If it is difficult for this to make metal of sufficient quantity for improvement in activity support if mean particle diameter tends to control to 2 nm or less and mean particle diameter is not less than 10 nm, It is because coverage of metal particles to a titanium oxide particle surface will increase, an active site on the surface of titanium oxide will be covered and improvement in activity becomes small.

[0015] Mean particle diameter said here refers to a value of an average of particle diameter of 500 metal particles measured by product HF made from transmission electron microscope HITACHI-2000 by one about 2,500,000 times the magnification of this. The diameter was made into particle diameter when metal particles were circular. When metal particles were not circular, it was considered as particle diameter with a diameter of circle (projected area diameter) of the same area as the project area. Although CVD methods, such as PVD and plasma CVD method like a vacuum deposition method or a sputtering technique, and a heat CVD method, are known, a metal support method has a simple photoreduction method, and it is desirable. A photoreduction method puts a thing of a method of returning and supporting a metal ion by applying a metallic salt solution to a titanium oxide thin film, and irradiating with ultraviolet radiation. When performing a photoreduction method, since the metal source can remove a conjugate base easily from a catalyst surface as carbon dioxide by optical exposure, a catalyst does not carry out poisoning of it, and since acquisition is also easy, acetate is preferred [the metal source], although it is usable in a chloride, a nitrate, etc.

[0016] Ultraviolet radiation light sources, such as xenon light, a high-pressure mercury-vapor lamp, germicidal lamp glass, and a black light, can be used for an optical exposure. An example of an ultraviolet irradiation method in a photoreduction method is as follows. When ultraviolet ray intensity of 360 nm irradiated with light of a black light of $1 \text{ mW}\cdot\text{cm}^{-2}$ for 24 hours, metal salt which more than $5 \text{ pmol}\cdot\text{cm}^{-2}$ supported with density below 500

$\text{pmol}\cdot\text{cm}^{-2}$ was returned. More than $5.0\times 10^{-8}\text{mol}\cdot\text{L}^{-1}$ concentration of a metallic salt solution below $5.0\times 10^{-3}\text{mol}\cdot\text{L}^{-1}$. Spreading and desiccation are easy for below $5.0\times 10^{-6}\text{mol}\cdot\text{L}^{-1}$, and it is [more than $5.0\times 10^{-7}\text{mol}\cdot\text{L}^{-1}$] more preferably preferred also from a point of solubility of metal salt.

[0017]As for anatase type titanium oxide dispersion liquid containing a peroxo group for producing a titanium oxide thin film, it is preferred to be a mole ratio and to contain 5% or less of peroxo group 0.5% or more more preferably 10% or less 0.1% or more to Ti quantity. Photocatalyst activity durability not only after a thin film with it not being produced by a mole ratio but an end of an optical exposure also has a low peroxo group. [the bad dispersibility of sol and] [uniform in less than 0.1%] In being more than 10%, there is a possibility that the photocatalyst activity of a titanium oxide thin film may become low.

[0018]As for a titanium oxide thin film produced by producing anatase type titanium oxide dispersion liquid containing a peroxo group of the above-mentioned range at ordinary temperature, it is preferred to be a mole ratio and to contain 5% or less of peroxo group 10% or less of not less than 100 ppm 0.1% or more more preferably to Ti. If there are few peroxo groups at a mole ratio than 100 ppm, a metal ion supported by titanium oxide will be eluted easily. Peroxo radical weight which a titanium oxide thin film produced by producing anatase type titanium oxide dispersion liquid which contains anatase type titanium oxide dispersion liquid or a peroxo group containing a peroxo group in this invention contains, It can quantify in accordance with the iodometry method widely used as assay of a peroxo group.

[0019]As for thickness of a titanium oxide thin film, 0.01 micrometers or more 3 micrometers or less are preferred, and it is 0.1 micrometers or more 2 micrometers or less more preferably. Photocatalyst activity of less than 0.01 micrometer is not enough as thickness, and thickness becomes easy to produce a crack in not less than 3 micrometers. In this way, since metal particles currently supported by titanium oxide thin film promote charge separation of an electron generated to a titanium oxide thin film, and an electron hole, the photocatalyst thin film by obtained this invention can improve photocatalyst activity.

[0020]Since anatase type titanium oxide dispersion liquid containing a peroxo group is being used for this photocatalyst thin film as titanium oxide photocatalyst coating liquid, it can adopt a base of construction material broad as a base, and can be produced at ordinary temperature. Since metale support can also be performed using solution at ordinary temperature, this photocatalyst thin film can be manufactured simply and safely at ordinary temperature. In order to harden a titanium oxide thin film produced by producing anatase type titanium oxide dispersion liquid containing a peroxo group in a base surface, without calcinating, it has high surface area. In addition to it, for a ***** reason produced without being calcinated, a peroxo group of most which was contained in dispersion liquid is not disassembled, but it has the character which is not in other titanium oxide thin films of remaining in a titanium oxide thin film.

[0021]When this photocatalyst thin film is used underwater, metale elution is hardly seen. Since a peroxo group contained in a thin film since many sites where a titanium oxide thin film mentioned above has high surface area besides a reason very few metale holding amounts are, as this reason, and metal is fixed exist is charged in negative, Even if a metal ion which is a positive ion arises, electrostatic attraction works between peroxo

groups, and it seems that it is because there is an effect which prevents elution of a metal ion.

[0022]

[Embodiment of the Invention]The amount of titanium in the anatase type titanium oxide dispersion liquid containing the peroxo group in this invention was calculated by product JY made from ICP AEM device JYOBIN YVON138UL TRACE. The amount of titanium contained in the titanium oxide thin film which produced the anatase type titanium oxide dispersion liquid containing the peroxo group in this invention was calculated by RIX3000 made from fluorescence-X-rays measuring device RIGAKU.

[0023]All the fixed quantity of the peroxo group in the titanium oxide thin film which produced the anatase type titanium oxide dispersion liquid containing the anatase type titanium oxide dispersion liquid and the peroxo group containing the peroxo group in this invention was performed by the iodometry method as follows. 1 ml of acetic acid in 1 ml of saturated sodium iodide solutions, and the added solution at 25 ml of isopropanol which removed dissolved oxygen using dry ice beforehand as a sample, In the case of the anatase type titanium oxide dispersion liquid containing a peroxo group, about 10 ml is exfoliated, in the case of a titanium oxide thin film, about 50 mg is exfoliated, and it adds, and it is kept warm at 40 °C for 1 hour, and iodine ion is made to react to the hyperoxidation group which remains enough, and the liquid which carried out coloration by iodine I_2 to generate is obtained. Subsequently, it titrates using a 0.01-mol sodium subsulfite solution, and the place which becomes water-white is made into a terminal point. Hyperoxidation radical weight was calculated from the amount of sodium subsulfite which titration took, and the ratio of hyperoxidation radical weight to titanium was further computed from the amount of titanium in liquid.

[0024]The mean particle diameter of metal particles points out the value of an average of the particle diameter of 500 metal particles measured by product HF made from transmission electron microscope HITACHI-2000 by one about 2,500,000 times the magnification of this. The diameter was made into particle diameter when metal particles were circular. When metal particles were not circular, it was considered as particle diameter with the diameter of circle (projected area diameter) of the same area as the project area.

[0025]

[Example 1] The anatase type titanium oxide dispersion liquid (the product made from the Tanaka transfer, a trade name "TO sol") containing the commercial peroxo group which contains 2.0% of peroxo group by a mole ratio is used to Ti. The coat of the 0.2-micrometer-thick titanium oxide thin film was carried out to 2.5 cm long, 5 cm wide, and a 2-mm-thick boro-silicated glass board (a shot made in Japan, trade name "Tempax"). This titanium oxide thin film contained 1.8% of peroxo group by the mole ratio to Ti. 0.3 ml of copper acetate solution of 1.0×10^{-6} mol- L^{-1} was applied to this whole Tempax board surface. It irradiated with the black light light of 360-nm ultraviolet-ray-intensity 1 mW- cm^{-2} after spreading for 24 hours, and the sample A was obtained. The mean particle diameter of the copper grain child of this sample A was 4 nm.

[0026]The decomposition activity of acetaldehyde was measured with a circulation type photocatalysis device using this sample. The ceiling placed horizontally the breadth of 5 cm, 20 cm long, and the 6-mm-high reaction cell which were made from the window made from quartz, and placed the sample A in the center. Letting the window of a

reaction cell ceiling pass and irradiating with the light of the black light blue fluorescent lamp of ultraviolet-ray-intensity $3.5 \text{ mW}\cdot\text{cm}^{-2}$ from the upper part. 20% of oxygen, 80% of nitrogen, 1.5% of a steam, and the reactant gas that consists of acetaldehyde 10ppm were passed by flow $100 \text{ ml}\cdot\text{min}^{-1}$, and was made to react at the temperature of 25°C . When a reaction reached regularly, the acetaldehyde concentration of the reaction cell exit was 4.0 ppm, and carbon dioxide levels were 12 ppm. Although the sample A after a reaction was immersed in 100 ml of pure water for ten days, underwater copper ion concentration was 10 ppb or less. The activity of the sample A after immersion was equal before immersion.

[0027]

[Example 2] 0.3 ml of nickel acetate solution of $1.0\times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ was applied, and also the sample B was obtained like Example 1. The mean particle diameter of the nickel particle of this sample B was 5 nm. The decomposition activity of acetaldehyde was measured by the same method as Example 1 using this sample. When a reaction reached regularly, the acetaldehyde concentration of the reaction cell exit was 4.2 ppm, and carbon dioxide levels were 12 ppm. Although the sample B after a reaction was immersed in 100 ml of pure water for ten days, underwater nickel ion concentration was 10 ppb or less. The activity of the sample B after immersion was equal before immersion.

[0028]

[Example 3] 0.3 ml of silver acetate solution of $1.0\times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ was applied, and also the sample C was obtained like Example 1. The mean particle diameter of the silver granule child of this sample C was 9 nm. The decomposition activity of acetaldehyde was measured by the same method as Example 1 using this sample. When a reaction reached regularly, the acetaldehyde concentration of the reaction cell exit was 4.9 ppm, and carbon dioxide levels were 10 ppm. Although the sample C after a reaction was immersed in 100 ml of pure water for ten days, underwater silver ion concentration was 10 ppb or less. The activity of the sample C after immersion was equal before immersion.

[0029]

[Example 4] 0.3 ml of chloroplatinic acid (IV) solution of $1.0\times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ was applied, and also the sample D was obtained like Example 1. The mean particle diameter of the platinum particles of this sample D was 10 nm. The decomposition activity of acetaldehyde was measured by the same method as Example 1 using this sample. When a reaction reached regularly, the acetaldehyde concentration of the reaction cell exit was 5.0 ppm, and carbon dioxide levels were 10 ppm. Although the sample D after a reaction was immersed in 100 ml of pure water for ten days, underwater platinum ion concentration was 10 ppb or less. The activity of the sample D after immersion was equal before immersion.

[0030]

[Example 5] 0.3 ml of cobaltous acetate solution of $1.0\times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ was applied, and also the sample E was obtained like Example 1. The mean particle diameter of the cobalt particle of this sample E was 8 nm. The decomposition activity of acetaldehyde was measured by the same method as Example 1 using this sample. When a reaction reached regularly, the acetaldehyde concentration of the reaction cell exit was 4.7 ppm, and carbon dioxide levels were 11 ppm. Although the sample E after a reaction was immersed in 100 ml of pure water for ten days, underwater cobalt ion concentration was 10 ppb or less. The activity of the sample E after immersion was equal before immersion.

[0031]

[Comparative example 1] The same TO sol as Example 1 was used, the coat of the 0.2-micrometer-thick titanium oxide thin film was carried out to 2.5 cm long, 5 cm wide, and the 2-mm-thick Tempax board, and the sample F was obtained. The decomposition activity of acetaldehyde was measured by the same method as Example 1 using this sample. When a reaction reached regularly, the acetaldehyde concentration of the reaction cell exit was 5.5 ppm, and carbon dioxide levels were 8.9 ppm. When it took out after the sample F after a reaction was immersed in 100 ml of pure water for ten days, and activity evaluation was carried out, activity was equal before immersion.

[0032]

[Effect of the Invention] Its photocatalyst activity is high, and its maintenance is good, and since the photocatalyst thin film of this invention has little underwater elution, it is useful to decomposition removal of an underwater malodorous substance among the air. Moreover, the photocatalyst thin film of this invention can be manufactured simply and safely at ordinary temperature on the surface of the base of broad construction material.

CLAIMS

[Claim(s)]

[Claim 1] To a titanium oxide thin film produced and made, anatase type titanium oxide dispersion liquid containing a peroxo group. A photocatalyst thin film currently more than $5 \text{ pmol}\cdot\text{cm}^{-2}$ supporting with density below $500 \text{ pmol}\cdot\text{cm}^{-2}$ at least one sort of metallic elements chosen from a group of Cu, Ag, Pt, Pd, nickel, Co, Fe, Ru, Zn, and Rh.

[Claim 2] A photocatalyst thin film of claim 1, wherein a titanium oxide thin film contains a peroxo group 10% or less of not less than 100 ppm by a mole ratio to Ti.

[Claim 3] The photocatalyst thin film according to claim 1 or 2, wherein metallic elements currently supported are with a 1-nm or more mean particle diameter [20 nm or less] metal particles.